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Kenyon, Ronald Wynford;

Assignee: **IMPERIAL CHEMICAL INDUSTRIES PLC**
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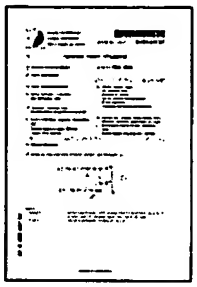
Priority Number: 1990-07-26 **GB1990000016448**



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Abstract:

Anionic azo compounds which, in the free acid form, have the Formula (1): wherein: Ar and Ar1are each independently aryl or substituted aryl providing at least one of Ar and Ar1 has at least one substituent selected from COOH and COSH; J and J1are each independently of formula (2), (3) or (4): each R5is independently selected from H, alkyl, substituted alkyl, alkoxy, halogen, CN, ureido and NHCOR6; R6is H, alkyl, substituted alkyl, aryl, substituted aryl, aralkyl or substituted aralkyl; each Tis independently alkyl; each Wis independently selected from H, CN, CONR10R11, pyridinium and COOH; each mis an alkylene chain having 2 to 8 carbon atoms; Bis H, alkyl or COOH; R1, Rý, R3, R4, R10 and R11are each independently H, alkyl or substituted alkyl; Lis a divalent organic linking group; nis 0 or 1; each Xis independently carbonyl or a group of the Formula (5), (6) or (7): Zis OR7, SR7 or NR8R9; Yis H, Cl, CN or Z; Eis Cl or CN; R7, R8 and R9are independently H, alkenyl, substituted alkenyl, alkyl, substituted alkyl, aryl, substituted aryl, aralkyl or substituted aralkyl, or R8 and R9 together with the nitrogen atom to which they are attached form a 5 or 6 membered ring; provided (i) if the compound of Formula (1) has no -SO3H groups then it has at least two groups selected from -COOH and -COSH; and (ii) the compound of Formula (1) has at least as many groups selected from -COOH and -COSH as -SO3H groups. The compounds are useful for the preparation of inks for use in ink-jet printing.

INPADOC Legal Status: Show legal status actions Get N w: Family Legal Status Report

Designated Country: AT BE CH DE ES FR GB GR IT LI LU NL SE

Family:

PDF	Publication	Pub. Date	Filed	Title
☒	US5374301	1994-12-20	1992-11-30	Inks suitable for use in ink jet printing
☒	US5268459	1995-05-09	1991-06-28	Azo dyes suitable for ink jet printing
☑	KR0153007B1	1998-11-02	1991-07-18	ANIONIC COMPOUNDS
☑	JP4233975A2	1992-08-21	1991-07-19	ANIONIC AZO COMPOUND
☑	JP3020658B2	2000-03-15	1991-07-19	
☑	HK0023397A	1997-02-27	1997-02-27	ANIONIC COMPOUNDS
	GB9114143A0	1991-08-21		
	GB9016448A0	1990-09-12		
☑	ES2084111T3	1996-05-01	1991-07-01	COMPUESTOS ANIONICOS.
☒	EP0468647B1	1996-03-13	1991-07-01	Anionic compounds
☒	**EP0468647A1**	1992-01-29	1991-07-01	Anionic compounds
☑	DE69117828T2	1996-09-19	1991-07-01	ANIONISCHE VERBINDUNGEN
☑	DE69117828C0	1996-04-18	1991-07-01	ANIONISCHE VERBINDUNGEN
☑	AU8017591A1	1992-08-13	1991-07-04	DISAZO HETEROCYCLIC COMPOUNDS
☑	AU0641782B2	1993-09-30	1991-07-04	DISAZO HETEROCYCLIC COMPOUNDS
☑	AT0135390E	1996-03-15	1991-07-01	ANIONISCHE VERBINDUNGEN
16 family members shown above				

Description: Expand full description

First Claim: Show all claims

1. An anionic azo compound which, in the free acid form, has the Formula (1): wherein:

Ar and Ar^1	are each independently aryl or substituted aryl providing at least one of Ar and Ar^1 has at least one substituent selected from COOH and COSH;
J and J^1	are each independently of formula (2), (3) or (4):
each R^5	is independently selected from H, alkyl, substituted alkyl, alkoxy, halogen, CN, ureido and $NHCOR^6$;
R^6	is H, alkyl, substituted alkyl, aryl, substituted aryl, aralkyl or substituted aralkyl;
each T	is independently alkyl;
each W	is independently selected from H, CN, $CONR^{10}R^{11}$, pyridinium and COOH;
each m	is an alkylene chain having 2 to 8 carbon atoms;
B	is H, alkyl or COOH;
R^1, R^2, R^3, R^4, R^{10} and R^{11}	are each independently H, alkyl or substituted alkyl;
L	is a divalent organic linking group;
n	is 0 or 1;
each X	is independently carbonyl or a group of the Formula (5), (6) or (7):
Z	is OR^7, SR^7 or NR^8R^9;
Y	is H, Cl, CN or Z;
E	is Cl or CN;

R^7, R^8 and R^9	are independently H, alkenyl, substituted alkenyl, alkyl, substituted alkyl, aryl, substituted aryl, aralkyl or substituted aralkyl, or R^8 and R^9 together with the nitrogen atom to which they are attached form a 5 or 6 membered ring; provided (i) if the compound of Formula (1) has no $-SO_3H$ groups then it has at least two groups selected from -COOH and -COSH; and (ii) the compound of Formula (1) has at least as many groups selected from -COOH and -COSH as $-SO_3H$ groups.

Forward References:

Go to Result Set: Forward references (8)

PDF	Patent	Pub.Date	Inventor	Assignee	Title
	US6590082	2003-07-08	Banning; Jeffrey H.	Xerox Corporation	Azo pyridone colorants
	US6576747	2003-06-10	Carlini; Rina	Xerox Corporation	Processes for preparing dianthranilate compounds and diazopyridone colorants
	US6576748	2003-06-10	Carlini; Rina	Xerox Corporation	Method for making dimeric azo pyridone colorants
	US6551390	2003-04-22	Lavery; Aidan Joseph	Avecia Limited	Composition containing two different disazodyestuffs useful for ink jet recording
	US6290763	2001-09-18	Millard; Christine	Zeneca Limited	AZO dyes and compositions comprising such dyes
	US5728201	1998-03-17	Saito; Eriko	Canon Kabushiki Kaisha	Ink, and ink-jet recording method and instruments using the same
	US5609673	1997-03-11	Takimoto; Hiroshi	Mitsubishi Chemical Corporation	Recording liquid
	US5451251	1995-09-19	Mafune; Kumiko	Canon Kabushiki Kaisha	Ink, and ink-jet recording method and instrument using the same

Other Abstract Info: None

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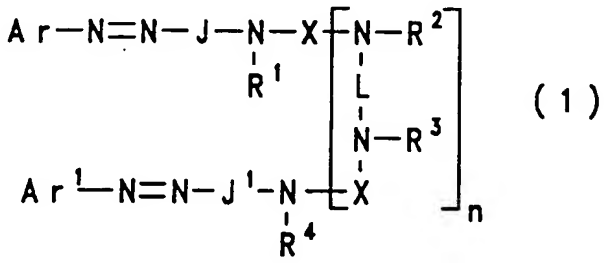
(54) Anionic compounds.

(57) Anionic azo compounds which, in the free acid form, have the Formula (1):



(1)

wherein:

Ar and Ar¹ are each independently aryl or substituted aryl providing at least one of Ar and Ar¹ has at least one substituent selected from COOH and COSH;

J and J¹ are each independently of formula (2), (3) or (4):

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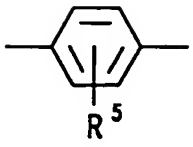

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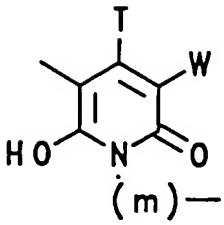

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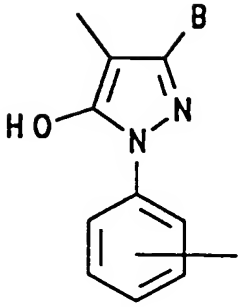
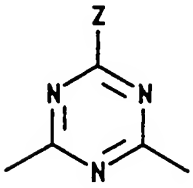


(4)

each R^5	is independently selected from H, alkyl, substituted alkyl, alkoxy, halogen, CN, ureido and $NHCOR^6$;
R^6	is H, alkyl, substituted alkyl, aryl, substituted aryl, aralkyl or substituted aralkyl;
each T	is independently alkyl;
each W	is independently selected from H, CN, $CONR^{10}R^{11}$, pyridinium and COOH;
each m	is an alkylene chain having 2 to 8 carbon atoms;
B	is H, alkyl or COOH;
R^1, R^2, R^3, R^4, R^{10} and R^{11}	are each independently H, alkyl or substituted alkyl;
L	is a divalent organic linking group;
n	is 0 or 1;
each X	is independently carbonyl or a group of the Formula (5), (6) or (7):



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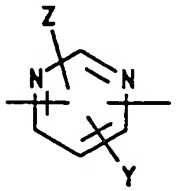

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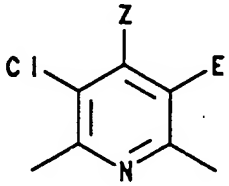


(7)

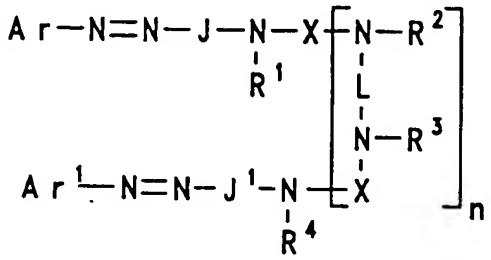
Z	is OR^7, SR^7 or NR^8R^9;
Y	is H, Cl, CN or Z;
E	is Cl or CN;
R^7, R^8 and R^9	are independently H, alkenyl, substituted alkenyl, alkyl, substituted alkyl, aryl, substituted aryl, aralkyl or substituted aralkyl, or R^8 and R^9 together with the nitrogen atom to which they are attached form a 5 or 6 membered ring;

provided (i) if the compound of Formula (1) has no $-SO_3H$ groups then it has at least two groups selected from -COOH and -COSH; and (ii) the compound of Formula (1) has at least as many groups selected from -COOH and -COSH as $-SO_3H$ groups.

The compounds are useful for th preparation of inks for use in ink-jet printing.

This specification describes an invention relating to anionic compounds and particularly to anionic azo compounds which are useful as the coloured component of inks, particularly inks used in ink jet printing.

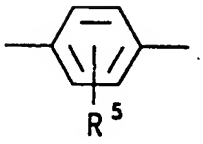
According to the present invention there are provided anionic azo compounds which, in the free acid form, have the structure shown in Formula (1):



(1)

wherein:

Ar and Ar^1	are each independently aryl or substituted aryl providing at least one of Ar and Ar^1 has at least one substituent selected from COOH and COSH;
J and J^1	are each independently of formula (2), (3) or (4):



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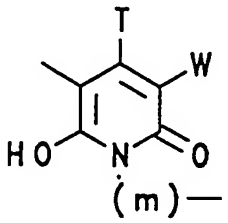

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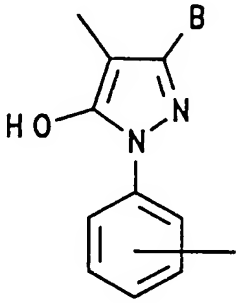
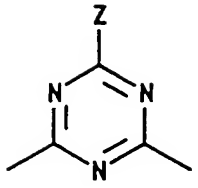
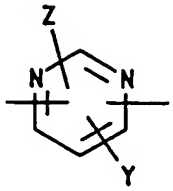
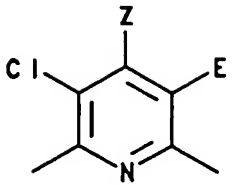


(4)

each R^5	is independently selected from H, alkyl, substituted alkyl, alkoxy, halogen, CN, ureido and $NHCOR^6$;
R^6	is H, alkyl, substituted alkyl, aryl, substituted aryl, aralkyl or substituted aralkyl;
each T	is independently alkyl;
each W	is independently selected from H, CN, $CONR^{10}R^{11}$, pyridinium and COOH;
each m	is an alkylene chain having 2 to 8 carbon atoms;
B	is H, alkyl or COOH;
R^1, R^2 R^3, R^4, R^{10} and R^{11}	are each independently H, alkyl or substituted alkyl;
L	is a divalent organic linking group;
n	is 0 or 1;
each X	is independently carbonyl or a group of the Formula (5), (6) or (7):







(5) (6) (7)

Z	is OR^7, SR^7 or NR^8R^9;
Y	is H, Cl, CN or Z;
E	is Cl or CN;
R^7, R^8 and R^9	are independently H, alkenyl, substituted alkenyl, alkyl, substituted alkyl, aryl, substituted aryl, aralkyl or substituted aralkyl, or R^8 and R^9 together with the nitrogen atom to which they are attached form a 5 or 6 membered ring;

provided (i) if the compound of Formula (1) has no $-SO_3H$ groups then it has at least two groups selected from -COOH and -COSH; and (ii) the compound of Formula (1) has at least as many groups selected from -COOH and -COSH as SO_3H groups.

It is preferred that the compound of Formula (1) has at least as many -COOH as $-SO_3H$ groups and if the compound of Formula (1) has no $-SO_3H$ groups then it has at least two and more preferably at least three -COOH groups.

It is preferred that Ar-N=N-J and Ar-N=N-J^1 are such that the compounds of Formula (1) are yellow. It is also preferred that compounds of Formula (1) are free from cellulose reactive groups.

The groups Ar and Ar^1 are preferably independently selected from naphthyl, substituted naphthyl, phenyl and substituted phenyl, especially phenyl and substituted phenyl. The optional substituents on Ar and Ar^1 are preferably selected from alkyl, especially C_{1-4}-alkyl; substituted C_{1-4}-alkyl; alkoxy, especially C_{1-4}-alkoxy; $-SO_3H$; $-PO_3H_2$; -COSH; -OH; $-CO_2H$; halogen, especially Cl or Br. It is particularly preferred that when Ar and Ar^1 are substituted the substituents are independently selected from CO_2H, COSH and SO_3H, especially CO_2H. In especially preferred structures, at least one of Ar and Ar^1 has at least one -COOH substituent but it is even more preferred that each of Ar and Ar^1 has at least one -COOH substituent and more particularly at least two -COOH substituents as in, for example, dicarboxyphenyl.

Each R^5 is preferably independently selected from H, C_{1-4}-alkyl, substituted C_{1-4}-alkyl, C_{1-4}-alkoxy, Cl, CN, Br, ureido or $NHCOR^6$, more preferably H, C_{1-4}-alkyl, C_{1-4}-alkoxy, ureido or $NHCO(C_{1-4}$-alkyl), especially H, methyl, methoxy or ureido. Each R^5 is preferably ortho with respect to the azo group connected to the same ring.

R^6 is preferably H, C_{1-4}-alkyl, phenyl or $(CH_2)_{1-4}$-phenyl, all of which are either unsubstituted or substituted. R^6 is more preferably C_{1-4}-alkyl.

Each T is preferably independently C_{1-6}-alkyl, especially C_{1-4}-alkyl.

The group (m) present in Formula (3) is branched chain alkylene or preferably straight chain alkylene.

B is preferably H.

When X is of Formula (6) it is preferred that Z is attached to the carbon atom between the two ring nitrogen atoms and that Y is para with respect to Z. Each X independently is preferably of Formula (5).

Z is preferably NR^8R^9, especially NHC_2H_4OH, $N(C_2H_4OH)_2$, morpholino, $NH(C_{1-6}$-alkyl), $NH-(CH_2)_2-CO_2H$, $NHCH_2C_6H_4CO_2H$, mono- or di-carboxyanilino, $NHC_6H_4SO_3H$ or $NHCH_2SO_3H$.

R^1, R^2, R^3 and R^4 are preferably independently selected from H, C_{1-4}-alkyl and C_{1-4}-alkyl substituted by OH.

R^7, R^8 and R^9 are preferably independently selected from H, C_{1-6}-alkyl, substituted C_{1-6}-alkyl, C_{3-4}-alkenyl, phenyl, substituted phenyl, $(CH_2)_{1-4}$-phenyl, substituted $(CH_2)_{1-4}$-phenyl, mor preferably H, allyl, C_{1-4}-alkyl, benzyl, hydroxy C_{1-4}-alkyl especially H, methyl, ethyl and 2-hydroxyethyl. The optional substituents on R^7, R^8 and R^9 are preferably independently selected from -OH, $-SO_3H$ and -COOH, specially -OH. When R^8 and R^9 together with the nitrogen atom to which they ar attached form a 5 or 6

memb red ring they preferably form a morpholine, piperazine or piperidine ring.

The identity f the dival nt organic linking group L is not critical providing it does not interfer with the performance of the compound. As examples of divalent organic linking groups represented by L there may be mentioned:

(a) divalent aliphatic radicals, preferably those containing from 2 to 6 carbon atoms, such as ethylene, trimethylene, propylene, tetramethylene, alpha:beta-dimethylethylene and hexamethylene radicals;

(b) divalent aromatic homocyclic radicals in which at least one of the terminal links is through an aliphatic carbon atom, for example as in the benzylene $-C_6H_4.CH_2-$ or the xylylene $-CH_2C_6H_4CH_2-$ group;

(c) divalent monocyclic or fused polycyclic aromatic radicals, for example of the benzene, naphthalene, anthraquinone or fluorene series, such as

1,3- or 1,4-phenylene	2-nitro-1,4-phenylene
3-sulpho-1,4-phenylene	4-methoxy-1,3-phenylene
4-sulpho-1,3-phenylene	4-nitro-1,3-phenylene
2-carboxy-1,4-phenylene	2-chloro-1,4-phenylene
4-carboxy-1,3-phenylene	3,7-disulpho-1,5-naphthylene
2-methoxy-1,4-phenylene;	

(d) divalent radicals wherein the terminal bonds are attached to carbon atoms of two phenyl or naphthalene nuclei which are joined together either through a direct link or through an atom or chain of atoms which may form a homocyclic or heterocyclic ring. Of this type, there may be mentioned as examples divalent radicals derived from

diphenyl	azobenzene
diphenyloxide	diphenyloxadiazole
diphenylamine	benzanilide
diphenylsulphide	diphenylurea
diphenylsulphone	1,2-bis(phenylcarbamyl)ethylene
diphenylmethane	1,4-bis-(phenylcarbamyl)butadiene
diphenylketone	1,2-bis-(phenylcarbamyl)ethane
diphenylethane	1,3-bis-(phenylcarbamyl)propane
diphenylethylene	2,4-dianilino-s-triazine;

and

(e) nuclear substituted derivatives of the above, for example, containing COOH, methyl, nitro and/or sulphonic acid and/or chlorine atoms as substituents in the phenyl or naphthalene nuclei.

Alternatively the group NR^2LNR^3 can be piperazino in which the two ring nitrogen atoms are bonded to the groups represented by X.

It is to be understood that the present invention relates not only to compounds of Formula (1) but also to the salts thereof, particularly the salt with an alkali metal, ammonia or substituted amines, especially ammonia and substituted amines which are volatile at room temperature. It is also to be understood that whilst Formulae (3) and (4) above are represented in neutral form, the present invention also covers quaternary salts of Formulae (3) and (4), particularly when the compound of Formula (1) is in zwitterionic form.

According to a further aspect of the present invention there is provided a process for the preparation of compounds of Formula (1) comprising

(i) diazotisation of amines of the formulae $ArNH_2$ and Ar^1NH_2 with a diazotising agent such as HNO_2, in the cold and preferably below 5° C to give the corresponding diazonium salts;

(ii) coupling the diazonium salt formed from $ArNH_2$ with an amine of l formula H - J - NR^1H, and coupling the diazonium salt formed from Ar^1NH_2 with an amine of formula H - J^1 - NR^4H to give monoazo amines;

(iii) reacting the monoazo amines of step (ii) in either order or simultaneously with a compound of formula

Cl - X - (NR^2 - L - NR^3 - X)$_n$ - Cl, preferably in the presence of base; wherein Ar, Ar^1, X, R^1 to R^4, J, J^1, L and n are as defined above unless stated otherwise.

Alternatively, step (iii) may be followed except that in the definition of X above, instead of the substituent Z there is Cl, and th pr duct of step (iii) is react d with a compound of formula ZH (wher in Z

is as hereinbefore defined) to give a compound of Formula (1).

As Examples of amines of formulae $ArNH_2$ and Ar^1NH_2 which may be used in the preparation of compounds of Formula (1), there may be mentioned

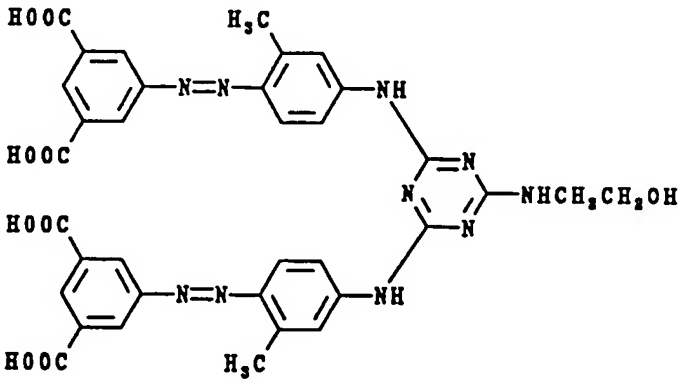
2-aminoisophthalic acid	3-amino-4-fluorobenzoic acid
4-aminoisophthalic acid	3-amino-5-hydroxybenzoic acid
5-aminoisophthalic acid	3-amino-4-hydroxybenzoic acid
3-aminophthalic acid	3-amino-2-hydroxybenzoic acid
4-aminophthalic acid	2-amino-6-hydroxybenzoic acid
2-aminoterephthalic acid	2-amino-4-nirobenzoic acid
3-aminobenzoic acid	3-amino-5-nitrobenzoic acid
4-aminobenzoic acid	2-nitro-3-aminobenzoic acid
anthranilic acid	2-nitro-5-aminobenzoic acid
4-sulphoanthranilic acid	3-nitro-4-aminobenzoic acid
5-sulphoanthranilic acid	3-acetylamino-5-aminobenzoic acid
2-amino-4-chlorobenzoic acid	3-amino-4-methylbenzoic acid
2-amino-5-chlorobenzoic acid	2-amino-3-methylbenzoic acid
3-amino-4-chlorobenzoic acid	3-amino-4-methoxybenzoic acid
5-amino-2-chlorobenzoic acid	3-amino-4-hydroxybenzoic acid
2-amino-5-methylbenzoic acid	4-aminosalicylic acid
2-amino-6-methylbenzoic acid	5-aminosalicylic acid
2-amino-5-bromobenzoic acid	3-amino-2-naphthoic acid
2-n-butoxy-4-aminobenzoic acid	5-amino-2-naphthoic acid
	8-amino-2-naphthoic acid

The compounds of Formula (1) are especially useful for the preparation of inks, especially aqueous inks, used in ink jet printing and particularly thermal ink jet printing. The inks can be prepared according to known formulations.

The invention is further illustrated by the following Examples in which all parts and percentages are by weight unless otherwise indicated.

Example 1

Preparation of



5-aminoisophthalic acid (36.2g) was stirred in water (1 litre) and the pH adjusted to 8-9 by addition of 2N sodium hydroxide. Sodium nitrite (14g) was added and the solution added to a mixture of concentrated hydrochloric acid (60ml) and water (500ml) at 0-10°C. After 1 hour at 0-10°C the excess nitrous acid was removed by addition of a little sulphamic acid, to give a diazo suspension.

m-toluidine (21.4g) was added to water (500ml) and concentrated hydrochloric acid (25ml) added. The solution was added over ½ hour to the above diazo suspension at 0-10°C. The pH was adjusted to 4.0 by

addition of 47% sodium hydroxide solution and the mixtur stirred for 18 hours at 0-10°C. The pH was adjusted to 8.0 with 47% sodium hydroxide solution, screened and then warmed to 60°C. It was slowly acidified to pH 4.0 with concentrated hydrochloric acid and the product filtered, washed with water and dried to give a monoazo compound.

8.87g (one equivalent) of the above monoazo compound was added to water (500ml) and the pH adjusted to 8.0 by addition of 47% sodium hydroxide solution. It was cooled to 0-10°C and a solution of cyanuric chloride (4.61g, one equivalent) in acetone (50ml) added maintaining the pH at 7-8 and a temperature of 0-10°C. After ½ hour a further solution of one equivalent of the above monoazo compound (8.87g) in water (500ml) at pH 8.0 was added and the reaction mixture warmed to 45°C and stirred at this temperature for 4 hours maintaining the pH at 7-8.

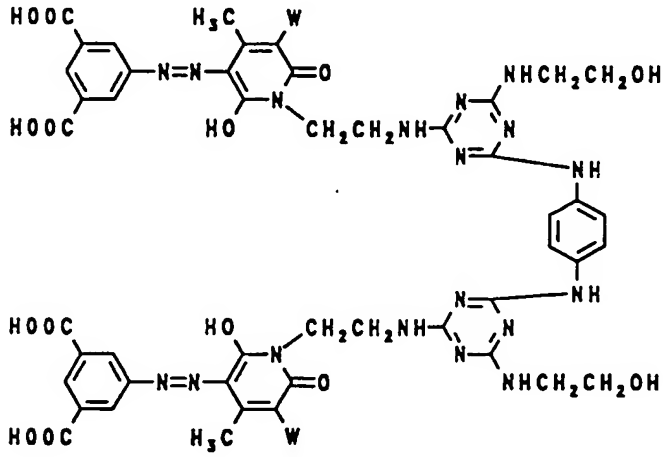
2-Aminoethanol (10g) was then added and the mixture heated to 80°C. After stirring at 80°C for 2 hours the pH was adjusted to 7.0 and salted to 20% using sodium chloride. The product was filtered and washed with saturated brine.

The above product was dissolved in water (1 litre) and the solution added to 2N hydrochloric acid to precipitate the title product in free acid form. The title product was filtered, washed and added to water (200ml). The pH was adjusted to 9.0 with concentrated ammonium hydroxide and the solution dialysed to remove chloride ions, screened and evaporated to give the ammonium salts of the title product. Yield =, 10g.

When made into an ink by dissolving in water/diethylene glycol (92.5/7.5) and printed onto plain paper using a thermal ink-jet printing machine the ammonium salt of the title compound gave bright yellow shades with excellent water fastness and good light fastness. The same water/diethylene glycol mixture was used as the solvent in the inks described in subsequent Examples.

Example 2

Preparation of the compound of Formula (8) in which W is H



(8)

5-aminoisophthalic acid (9.05g) was stirred in water (150ml) and the pH adjusted to 8-9 by addition of 2N sodium hydroxide solution. 2N Sodium nitrite (25ml) was added and the solution added to a mixture of concentrated hydrochloric acid (25ml) and water (200ml) at 0-5°C. After 2 hours the excess nitrous acid was removed by addition of a little sulphamic acid, to give a a solution of diazonium salt.

A mixture of 1-(2-aminoethyl)-6-hydroxy-4-methylpyrid-2-one (8.4g), water (300ml), sodium acetate (12.5g) and 2N sodium hydroxide (40ml) was stirred at 0-5°C and the above solution of diazonium salt added at 0-5°C. The mixture was stirred for 18 hours at 0-5°C. It was filtered, washed with water and dried to give 20.5g of azo pyridone compound.

18.0g of the above azo pyridone compound was stirred in water (300ml) and cooled to 0-5°C. A solution of cyanuric chloride (10g, one equivalent) in acetone (100ml) was added at 0-5°C maintaining the pH at 7-8 by addition of 2N sodium hydroxide. After 3 hours the temperature was raised to 20-25°C and a

solution of 1,4-phenylenediamine (2.16g, ½ equivalent) in acetone (25ml) added, maintaining the pH at 7-8. The mixture was stirred for 18 hours at 20-25° C maintaining the pH at 7-8.

The mixture was then acidified to pH 5 with concentrated hydrochloric acid, filtered, washed and dried to give 24.6g of a bis(monochlorotriazine) interm diate compound.

11.46g of the bis(monochlorotriazine) intermediate compound was stirred in water (150ml) and 2-aminoethanol (9.2g) added. The mixture was heated to 65° C and stirred at 65-70° C for 12 hours. It was then acidified to pH 5, sodium chloride (30g) added, and the product filtered off.

The product was then added to water (150ml) and the pH adjusted to 9.0 with sodium hydroxide solution. The solution was added to a mixture of concentrated hydrochloric acid (20ml) and water (200ml) to precipitate the title compound in free acid form.

The title compound was filtered off and converted to the ammonium salt by adding to water (250ml) and adjusting the pH to 9.0 by addition of concentrated ammonium hydroxide.

The solution was dialysed to remove chloride ions, screened and evaporated to give the ammonium salt of the title compound. Yield = 8.0g.

When made into an ink and printed onto plain paper using a thermal ink-jet printing machine the ammonium salt of the title compound gave bright yellow shades with excellent water fastness and good light fastness.

Example 3

Preparation of the compound of Formula (8) in which W is CN

In place of the 8.4g of 1-(2-aminoethyl)-6-hydroxy-4-methylpyrid-2-one used in Example 2 there was used 8.95g of 1-(2-aminoethyl)-3-cyano-6-hydroxy-4-methylpyrid-2-one. The ammonium salt of the title compound when made into an ink and printed onto plain paper using a thermal ink-jet printing machine gave yellow shades having excellent water fastness.

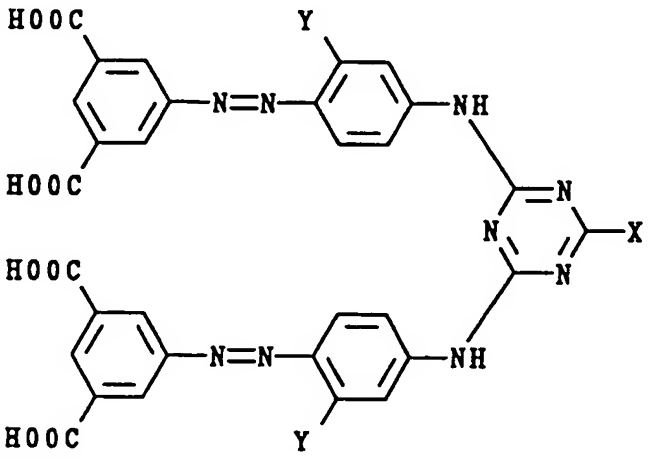
Example 4

Preparation of the compound of Formula (8) in which W is $CONH_2$

In place of the 8.4g of 1-(2-aminoethyl)-6-hydroxy-4-methylpyrid-2-one used in Example 2 there was used 10.55g of 1-(2-aminoethyl)-3-carbonamido-6-hydroxy-4-methylpyrid-2-one. The ammonium salt of the title compound when made into an ink and printed onto plain paper using a thermal ink-jet printing machine gave yellow shades having excellent water fastness.

Example 5

Preparation of the compound of Formula (9) in which X is $N(C_2H_4OH)_2$ and Y is CH_3



(9)

In place of the 10g of 2-aminoethanol used in Example 1 there was used 17.2g of diethanolamine. The ammonium salt of the title compound when made into an ink and printed onto plain paper using a thermal ink-jet printing machine gave yellow shades having excellent water fastness.

Example 6

Preparation of the compound of Formula (9) in which X is morpholino and Y is CH_3

In place of the 10g of 2-aminoethanol used in Example 1 there was used 14.3g of morpholine. The ammonium salt of the title compound when made into an ink and printed onto plain paper using a thermal ink-jet printing machine gave yellow shades having excellent water fastness.

Example 7

Preparation of the compound of Formula (9) in which X is OH and Y is CH_3

In place of the 10g of 2-aminoethanol used in Example 1 there was used 6.5g of sodium hydroxide. The ammonium salt of the title compound when made into an ink and printed onto plain paper using a thermal ink-jet printing machine gave yellow shades having excellent water fastness.

Example 8

Preparation of the compound of Formula (9) in which X is $NHCH_2CH_2OH$ and Y is H

5-Aminoisophthalic acid (36.2g) was diazotised as in Example 1.

Aniline ω-methane sulphonate (70g) was added to water (400ml) to dissolve. The solution was added to the above diazo suspension at 0-10°C and pH 7. The mixture was then stirred for 18 hours at 20°C.

The product was salted to 20% using sodium chloride, stirred for 2 hours, acidified to pH 4 with concentrated hydrochloric acid and then filtered.

The paste was added to a mixture of water (2 l) and sodium hydroxide (80g) and heated at 70-80°C for 3 hours. It was cooled to 20°C and salted to 20% using sodium chloride and acidified to pH 3 using concentrated hydrochloric acid. The product was filtered and dried to give the monoazo compound.

7.62g (one equivalent) of the above monoazo compound was added to water (500ml) and the pH adjusted to 8 by addition of 2N sodium hydroxide solution. It was cooled to 0-10°C and a solution of cyanuric chloride (50g; one equivalent) in acetone (50ml) added maintaining the pH at 7 and a temperature of 0-10°C. After 1 hour a further solution of one equivalent of the above monoazo compound (7.62g) in water (500ml) at pH 8.0 was added and the reaction mixture warmed to 30°C and stirred for 18 hours at 25-30°C. The pH was adjusted to 5.0 with concentrated hydrochloric acid and the product filtered.

It was slurried in water (500ml) and 2-aminoethanol (10g) added and the mixture heated to 80°C. After stirring at 80°C for 4 hours the product was salted to 30% with ammonium chloride and the mixture cooled to 20°C. The product was filtered and washed with saturated ammonium chloride solution.

The above product was dissolved in water (400ml) by addition of concentrated ammonium hydroxide solution and added to a mixture of water (200g) and concentrated hydrochloric acid (30g) to precipitate the title compound in free acid form. It was filtered, washed and added to water (200ml). The pH was adjusted to 9.0 with concentrated ammonium hydroxide solution and the solution dialysed to remove chloride ions, screened and evaporated.

The ammonium salt of the title compound when made into an ink and printed onto plain paper using a thermal ink jet printing machine gave bright yellow shades with very good water fastness.

Example 9

Preparation of the compound of Formula (9) in which X is $N(C_2H_4OH)_2$ and Y is H

In place of the 10g of 2-aminoethanol used in Example 8 there was used 15.75g of diethanolamine. The ammonium salt of the title compound when made into an ink and printed onto plain paper using a thermal ink-jet printing machine gave bright yellow shades with very good water fastness.

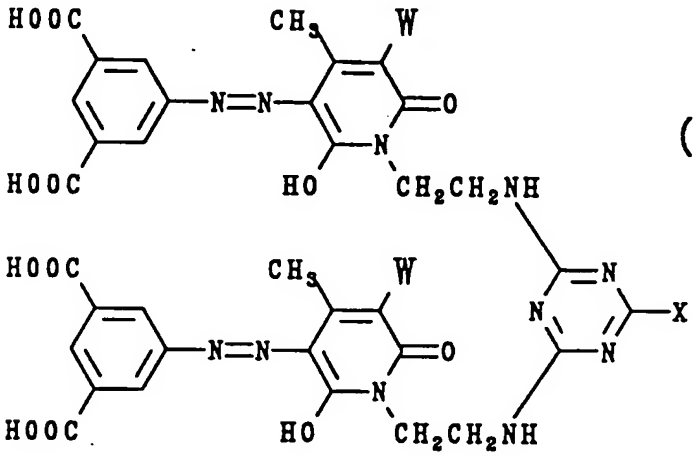
Example 10

Preparation of the compound of Formula (9) in which X is morpholino and Y is H

In place of the 10g of 2-aminoethanol used in Example 8 there was used 14.3g of morpholine. The ammonium salt of the title compound when made into an ink and printed onto plain paper using a thermal ink-jet printing machine gave bright yellow shades with very good water fastness.

Example 11

Preparation of the compound of Formula (10) in which W is H and X is $NHCH_2CH_2OH$



(10)

5-Aminoisophthalic acid was diazotised and coupled onto 1-(2-aminoethyl)-6-hydroxy-4-methylpyrid-2-one as in Example 2. It was then condensed with one equivalent of cyanuric chloride as in Example 2. A further equivalent of monoazo compound was then added, the temperature raised to 45°C and the pH maintained at 7-8 for 4 hours.

2-Aminoethanol (5g) was then added and the mixture heated at 65-70°C for 6 hours.

The reaction mixture was cooled to 20°C and the pH adjusted to 5 with concentrated hydrochloric acid. The product was filtered and reslurried in water (150ml) and the pH adjusted to 9.0 with sodium hydroxide solution. The solution was added to a mixture of water (200ml) and concentrated hydrochloric acid (20ml) to precipitate the title compound in free acid form.

It was filtered off and converted to the ammonium salt by adding to water (250ml) and adjusting the pH to 9.0 by addition of concentrated ammonium hydroxide.

The solution was dialysed to remove chloride ions, screened and evaporated.

When made into an ink and printed onto plain paper using a thermal ink jet printing machine it gave bright yellow shades with excellent water fastness.

Example 12

Preparation of the compound of Formula (9) in which X is $N(CH_3)C_2H_4OH$ and Y is H

In place of the 10g of 2-aminoethanol used in Example 8 there are used 12.3g of 2-(methylamino)-ethanol. The ammonium salt of the title compound when made into an ink and printed onto plain paper using a thermal ink-jet printing machine gives bright yellow shades with very good water fastness.

Example 13

Preparation of the compound of Formula (9) in which X is $N(C_2H_5)C_2H_4OH$ and Y is H

In place of the 10g of 2-aminoethanol used in Example 8 there are used 14.6g of 2-(ethylamino)ethanol. The ammonium salt of the title compound when made into an ink and printed onto plain paper using a

thermal ink-jet printing machine giv s bright yellow shades with very good water fastness.

Example 14

Preparation of the compound of Formula (9) in which X is $NH.nC_4H_9$ and Y is H

In place of the 10g of 2-aminoethanol used in Example 8 there was used 12g of n-butylamine. The ammonium salt of the title compound when made into an ink and printed onto plain paper using a thermal ink-jet printing machine gave bright yellow shades with very good water fastness.

Example 15

Preparation of the compound of Formula (9) in which X is $NH\text{-}nC_6H_{13}$ and Y is H

In place of the 10g of 2-aminoethanol used in Example 8 there was used 16.6g of n-hexylamine. The ammonium salt of the title compound when made into an ink and printed onto plain paper using a thermal ink-jet printing machine gave bright yellow shades with very good water fastness.

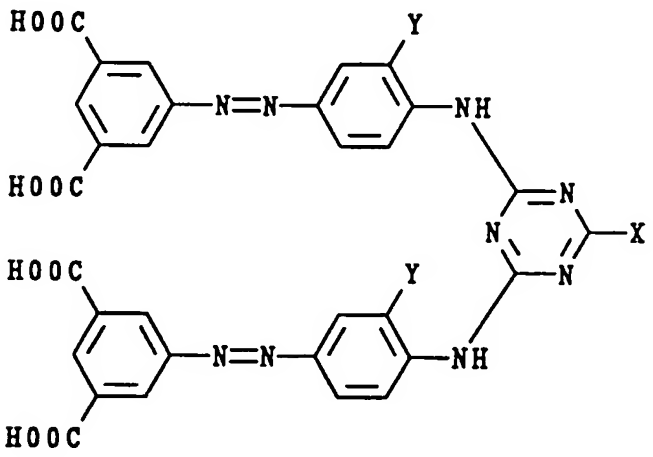
Example 16

Preparation of the compound of Formula (9) in which X is $NH(CH_2)_6OH$ and Y is H

In place of the 10g of 2-aminoethanol used in Example 8 there was used 19.2g of 6-amino-1-hexanol. The ammonium salt of the title compound when made into an ink and printed onto plain paper using a thermal ink-jet printing machine gave bright yellow shades with very good water fastness.

Example 17

Preparation of the compound of Formula (11) in which X is $NHCH_2CH_2OH$ and Y is OCH_3



(11)

In place of the 70g of aniline-ω-methane sulphonate used in Example 8 there was used 81.2g of o-anisidine-ω-methane sulphonate. The ammonium salt of the title compound when made into an ink and printed onto plain paper using a thermal ink-jet printing machine gave bright yellow shades with very good water fastn ss.

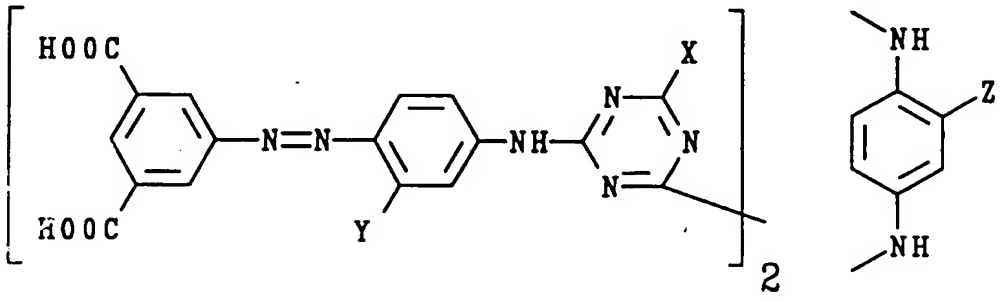
Example 18

Preparation of the compound of Formula (11) in which X is morpholino and Y is OCH_3

In place of th 10g of 2-aminoethanol used in Example 17 there was used 14.3g of morpholine. Th ammonium salt of the title compound when made into an ink and printed onto plain pap r using a thermal ink-jet printing machine gave bright yellow shades with good water fastness.

Example 19

Preparation of the compound of Formula (12) in which X is $NHCH_2CH_2OH$, Y is CH_3 and Z is H



(12)

The monoazo compound made by coupling diazotised 5-aminoisophthalic acid with m-toluidine was prepared as in Example 1. 22.4g of this monoazo compound was added to water (450ml) and the pH adjusted to 8.0 by addition of 47% sodium hydroxide solution. It was cooled to 0-10°C and a solution of cyanuric chloride (15g) in acetone (150ml) added maintaining the pH at 7-8 and a temperature of 0-10°C. After 3 hours a solution of p-phenylenediamine (3.24g) in acetone (30ml) was added and the reaction mixture stirred at 25°C and pH 7-8 for 18 hours. The reaction mixture was acidified to pH 5 with 2N hydrochloric acid and the product filtered off and pulled dry.

It was added to water (750ml) and 2-aminoethanol (27.6g) added. The temperature was raised to 65°C and stirred at 65-75°C for 6 hours. After cooling to 20°C the reaction mixture was acidified to pH 5 with concentrated hydrochloric acid and the title product filtered off. It was added to water (400ml) and the pH adjusted to 9.0 with concentrated ammonium hydroxide and the solution dialysed to remove chloride ions, screened and evaporated. The ammonium salt when made into an ink and printed onto plain paper using a thermal ink jet printer gave bright yellow shades with excellent water fastness.

Example 20

Preparation of the compound of Formula (12) in which X is $N(C_2H_4OH)_2$, Y is CH_3 and Z is H

In place of the 27.6g of 2-aminoethanol used in Example 19 there was used 47.5g of diethanolamine. The ammonium salt of the title compound when made into an ink and printed onto plain paper using a thermal ink-jet printing machine gave bright yellow shades with excellent water fastness.

Example 21

Preparation of the compound of Formula (12) in which X is morpholino, Y is CH_3 and Z is H

In place of the 27.6g of 2-aminoethanol used in Example 19 there was used 39.4g of morpholine. The ammonium salt of the title compound when made into an ink and printed onto plain paper using a thermal ink-jet printing machin gave bright y llow shades with excellent water fastness.

Example 22

Preparation of the compound of Formula (12) in which X is $NRCH_2CH_2OH$, and Y and Z are H

In place of the 22.4g of the monoazo compound used in Example 19 there was used 21.4g of the monoazo compound made by coupling diazotised 5-aminoisophthalic acid with aniline-ω-methane sulphonate followed by removal of the ω-methane sulphonate group as prepared in Example 8. When made into an ink and printed onto plain paper using a thermal ink-jet printing machine it gave bright yellow shades with very good water fastness.

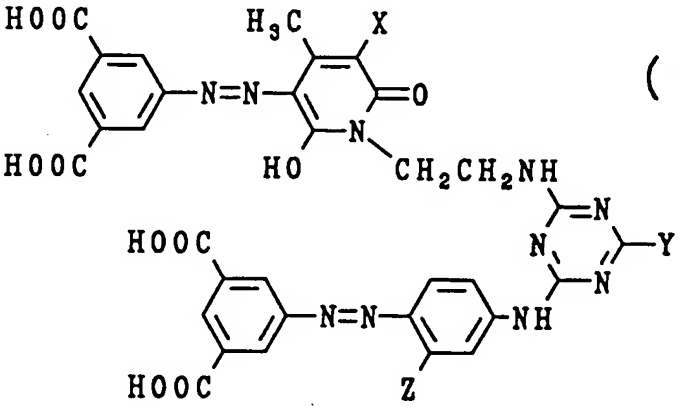
Example 23

Preparation of the compound of Formula (12) in which X is $N(C_2H_4OH)_2$, and Y and Z are H

In place of the 27.6g of 2-aminoethanol used in Example 22 there was used 47.5g of diethanolamine. The ammonium salt of the title compound when printed onto plain paper using a thermal ink-jet printing machine it gave bright yellow shades having good water fastness.

Example 24

Preparation of the compound of Formula (13) in which X is H, Y is $NHCH_2CH_2OH$, and Z is CH_3

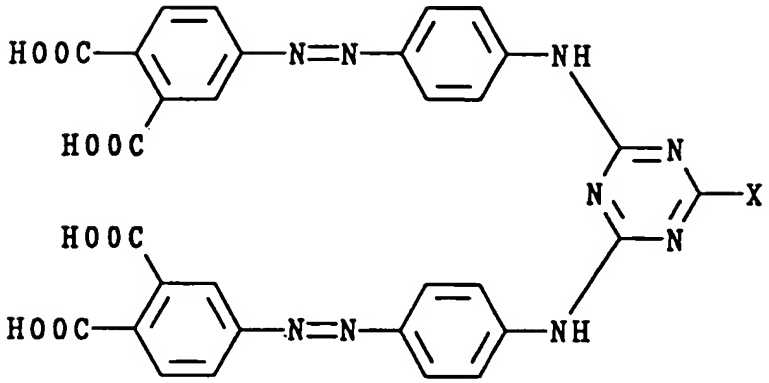


(13)

10.8g of the monoazo dye made by coupling diazotised 5-aminoisophthalic acid with 1-(2-aminoethyl)-6-hydroxy-4-methylpyrid-2-one prepared as in Example 2 was stirred in water (1 l) and the pH adjusted to 8.0. It was cooled to 0-5°C and a solution of cyanuric chloride (5.5g) in acetone (100ml) was added at 0-5°C maintaining the pH at 7-8 by addition of 2N sodium hydroxide. After 3 hours, 9g of the monoazo dye made by coupling 5-aminoisophthalic acid with m-toluidine prepared as in Example 1 was added and the mixture warmed to 40-45°C. It was stirred at this temperature, maintaining the pH at 7 for 4 hours. Ethanolamine (20g) was then added, the temperature raised to 80°C and stirred at this temperature for 2 hours. After cooling to 20°C it was acidified to pH 5 with concentrated hydrochloric acid and the product filtered off and padded dry. it was added to water (400ml) and the pH adjusted to 9 by addition of concentrated ammonium hydroxide. The solution was dialysed to remove chloride ions, screened and evaporated to give the ammonium salt of the title product. When made into an ink and printed onto plain paper using a thermal ink jet printer it gave bright yellow shades with very good water fastness.

Example 25

Preparation of the compound of Formula (14) in which X is morpholino

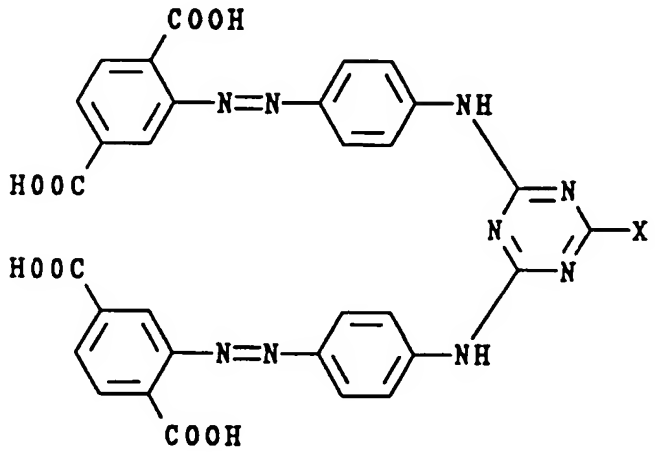


(14)

In place of the 5-aminoisophthalic acid used in Example 10 there is used an equal amount of 4-aminophthalic acid. The ammonium salt of the title compound when made into an ink and printed onto plain paper using a thermal ink-jet printing machine gives bright yellow shades having very good water fastness.

Example 26

Preparation of the compound of Formula (15) in which X is morpholino

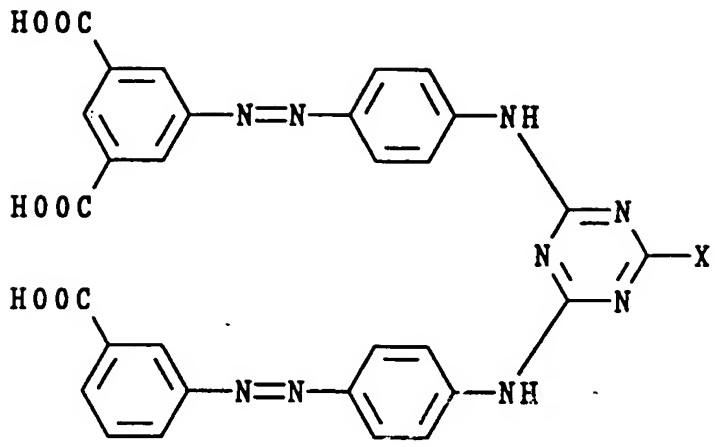


(15)

In place of the 5-aminoisophthalic acid used in Example 10 there is used an equal amount of 2-aminoterephthalic acid. The ammonium salt of the title compound when made into an ink and printed onto plain paper using a thermal ink-jet printing machine gives bright yellow shades having very good water fastness.

Example 27

Preparation of the compound of Formula (16) in which X is morpholino



(16)

3-Aminobenzoic acid (13.7g) is stirred in water (250ml) and the pH adjusted to 8-9 by addition of sodium hydroxide solution. Sodium nitrite (6.9g) is added and the solution added to a mixture of concentrated hydrochloric acid (20ml) and water (100ml) at 0-10°C. After 1 hour at 0-10°C, the excess nitrous acid is removed by addition of a little sulphamic acid.

Aniline ω-methane sulphonate (21g) is added to water (150ml) to dissolve. The solution is added to the above diazo solution at 0-10°C and pH 7. The mixture is stirred at 20°C for 18 hours. The product is salted to 20% using sodium chloride, stirred 1 hour and acidified to pH 4 with concentrated hydrochloric acid and then filtered.

The paste is added to a mixture of water (700ml) and sodium hydroxide (40g) and heated at 70-80°C for 3 hours. It is cooled to 20°C and salted to 20% using sodium chloride and acidified to pH 3 using concentrated hydrochloric acid. The product is filtered and dried to give the monoazo compound (A).

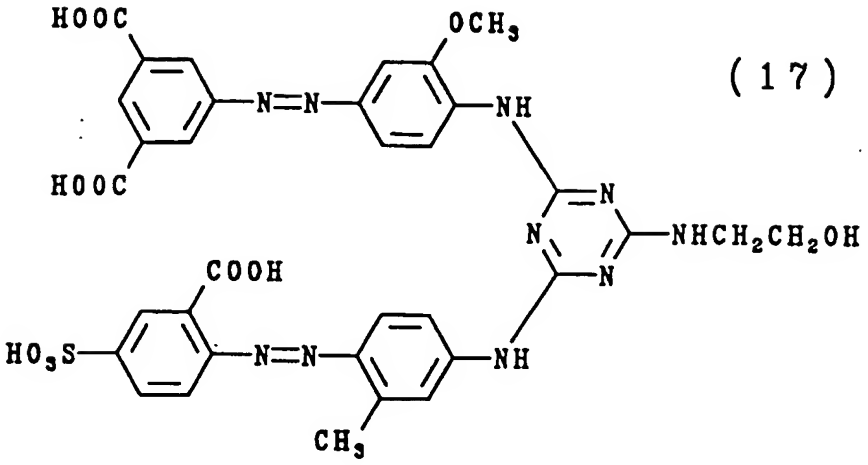
5-aminoisophthalic acid is diazotised and coupled onto aniline-ω-methane sulphonate as in Example 8. It is then heated with aqueous sodium hydroxide to remove the ω-methane sulphonate group as in Example 8 and 7.62g (1 equivalent) of this product condensed with cyanuric chloride as described in Example 8. After 1 hour, 6.5g (1 equivalent) of the above monoazo compound (A) in water (500ml) is added. The pH is adjusted to 8 and the reaction mixture stirred at 25-30°C for 18 hours. The pH is adjusted to 5.0 with concentrated hydrochloric acid and the product filtered.

The product is added to water (500g) and morpholine (14.3g) added and the mixture warmed to 80°C. After stirring at 80°C for 4 hours, the mixture is salted to 30% with ammonium chloride and then cooled to 20°C and filtered.

The ammonium salt when made into an ink and printed onto plain paper using a thermal ink jet printer gives bright yellow shades with very good water fastness.

Example 28

Preparation of the compound of Formula (17)



(17)

2-Amino-5-sulphobenzoic acid (21.7g) was added to a mixture of water (300ml) and concentrated hydrochloric acid (30ml) and the mixture cooled to 0-10°C. A solution of sodium nitrite (7.0g) in water (50ml) was added dropwise and the mixture stirred at 0-10 °C for 1 hour. The slight excess of nitrous acid was removed with sulphamic acid and then the mixture added slowly to a solution of m-toluidine (10.7g) in water (200ml) and concentrated hydrochloric acid (12.5ml) at 0-10°C. The pH was adjusted to 4.0 and the mixture stirred for 18 hours at 0-10°C. The monoazo compound was filtered off and dried.

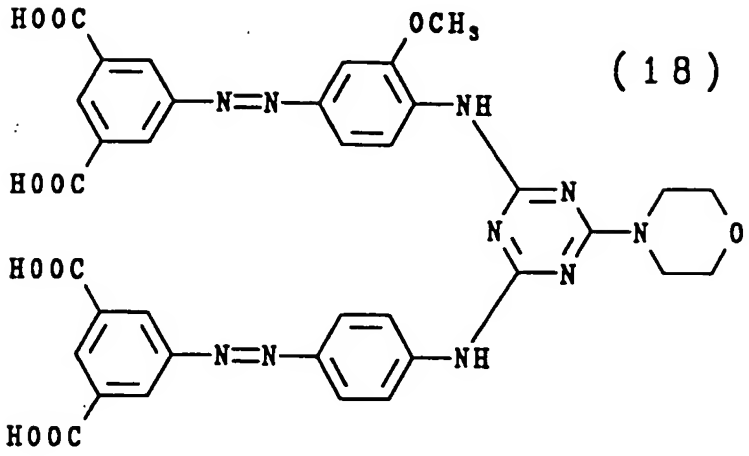
6.3g of the monoazo compound prepared from 5-aminoisophthalic acid and o-anisidine prepared as in Example 17 was added to water (500ml) and the pH adjusted to 8.0 by addition of 47% sodium hydroxide solution. It was cooled to 0-10°C and a solution of cyanuric chloride (3.69g) in acetone (50ml) was added maintaining the pH at 7-8 and a temperature of 0-10°C. After 30 minutes 6.7g of the monoazo compound prepared above from 2-amino-5-sulphobenzoic acid and m-toluidine in water (500ml) was added at pH 8.0 and the reaction mixture warmed to 40°C and stirred at this temperature for 4 hours maintaining the pH at 7-8.

2-Aminoethanol (8g) was then added and the mixture heated to 80°C. After stirring at 80°C for 4 hours the pH was adjusted to 7.0 and salted to 20% using sodium chloride. The product was filtered and washed with saturated brine.

It was converted to the ammonium salt as in Example 1, dialysed, screened and evaporated. When made into an ink and printed onto plain paper using a thermal ink jet printer it gave bright yellow shades with high water fastness.

Example 29

Preparation of the compound of Formula (18)



(18)

In place of the 6.7g of the monoazo compound derived from 2-amino-5-sulphobenzoic acid and m-toluidine used in Example 28 there is used 5.7g of the monoazo compound from 5-aminoisophthalic acid and aniline as prepared in Example 8 and in place of the 8g of 2-aminoethanol there is used 11g of morpholine. The ammonium salt of the title compound when made into an ink and printed onto plain paper using a thermal ink jet printing machine gives bright yellow shades with very good water fastness.

Example 30

Preparation of the compound of Formula (12) in which X is morpholino, Y is H and Z are CO_2H

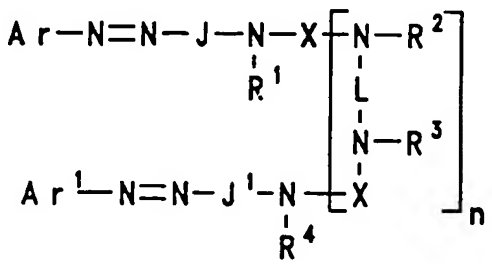
In place of the 3.24g of p-phenylenediamine used in Example 22 there is used 4.6g of 2,5-diaminobenzoic acid and in place of the 27.6g of 2-aminoethanol there is used 39.3g of morpholine. The ammonium salt of the title compound when made into an ink and printed onto plain paper using a thermal ink-jet printing machine gives bright yellow shades having high water fastness.

Example 31

In place of the 10g of 2-aminoethanol used in Example 1 there is used 10g of 4-(aminomethyl)benzoic acid. The product as the ammonium salt when made into an ink and printed onto plain paper using a thermal ink-jet printer gives bright yellow shades with excellent water fastness.

Claims

1. An anionic azo compound which, in the free acid form, has the Formula (1):



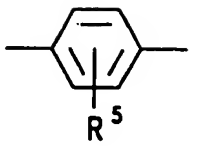
(1)

wherein:

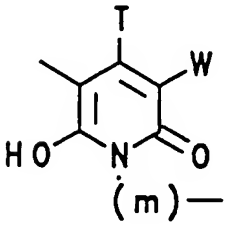
Ar and Ar^1 are each independently aryl or substituted aryl providing at least one of Ar and Ar^1 has at least one substituent selected from COOH and

COSH;

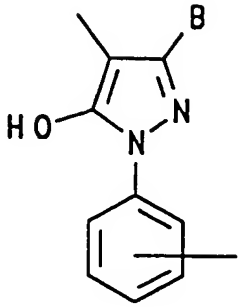
J and J[1] ar each independently of formula (2), (3) or (4):



(2)

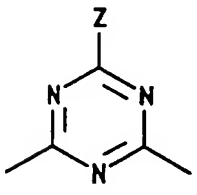


(3)

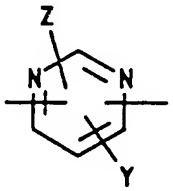


(4)

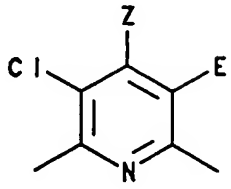
each R^5	is independently selected from H, alkyl, substituted alkyl, alkoxy, halogen, CN, ureido and $NHCOR^6$;
R^6	is H, alkyl, substituted alkyl, aryl, substituted aryl, aralkyl or substituted aralkyl;
each T	is independently alkyl;
each W	is independently selected from H, CN, $CONR^{10}R^{11}$, pyridinium and COOH;
each m	is an alkylene chain having 2 to 8 carbon atoms;
B	is H, alkyl or COOH;
R^1, R^2, R^3, R^4, R^{10} and R^{11}	are each independently H, alkyl or substituted alkyl;
L	is a divalent organic linking group;
n	is 0 or 1;
each X	is independently carbonyl or a group of the Formula (5), (6) or (7):



(5)



(6)



(7)

Z	is OR^7, SR^7 or NR^8R^9;
Y	is H, Cl, CN or Z;
E	is Cl or CN;
R^7, R^8 and R^9	are independently H, alkenyl, substituted alkenyl, alkyl, substituted alkyl, aryl, substituted aryl, aralkyl or substituted aralkyl, or R^8 and R^9 together with the nitrogen atom to which they ar attached form a 5 or 6 membered ring; provided (i) if the compound of Formula (1) has no $-SO_3H$ groups then it has at least two groups selected from -COOH and -COSH; and (ii) the compound of Formula (1) has at least

as many groups selected from -COOH and -COSH as $-SO_3H$ groups.

2. A compound according to Claim 1 having at least as many -COOH as $-SO_3H$ groups.

3. A compound according to Claim 1 having no $-SO_3H$ groups and at least two -COOH groups.

4. A compound according to Claim 3 having at least three -COOH groups.

5. A compound according to any preceding claim wherein at least one of the Ar and Ar^1 has at least one -COOH substituent.

6. A compound according to Claim 5 wherein each of Ar and and Ar^1 has at least one -COOH substituent.

7. A compound according to Claim 6 wherein each of Ar and and Ar^1 has at least two -COOH substituents.

8. A compound according to Claim 7 wherein each of Ar and and Ar^1 is dicarboxyphenyl.

9. A compound according to any preceding claim wheein X is a group of Formula (5) and Z is selected from $-NHC_2H_4OH$, $-N(C_2H_4OH)_2$, $-NH(C_{1-6}$-alkyl) and morpholino.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 91305940.8

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
A	US - A - 4 843 150 (HIHARA et al.) * Columns 35/36 : two formulae * --	1-7	C 09 B 62/00
A	US - A - 4 474 696 (TAKAHASHI et al.) * Claim 1 * ----	1	

TECHNICAL FIELDS SEARCHED (Int. Cl.5)

C 09 B
C 09 D

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
VIENNA	21-10-1991	HAUSWIRTH

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

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